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The Imide-Amide and Imide-Imide Rearrangements of Imidophosphorus Compounds

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Data on the imide-amide and imide-imide rearrangements of imidophosphorous compounds are surveyed, the factors influencing the ease of these rearrangements are noted, and information about their mechanisms is given. The bibliography includes 83 references.

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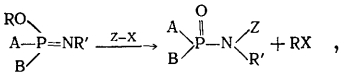
I. INTRODUCTION

Imidophosphorus compounds (IPC) containing at least one alkoxy-group at the phosphorous atom are as a rule converted into the corresponding amides on treatment with electrophiles. This reaction was observed in 1955 by Kabachnik and Gilyarov [1] and called the "imide-amide rearrangement". The centre of electrophilic attack in IPC may be not only the nitrogen atom (as in the imide-amide rearrangement) but also other atoms forming part of the conjugated system, for example, the oxygen atom of the carbonyl group in acetylimidophosphate [2] or the oxygen atom of the phosphoryl group in phosphorylimidophosphates [3], as well as the sulphur atom of thiophosphorylimidophosphates [4]. These reactions have been called the "imide-imide rearrangement" [5]. It is noteworthy that the majority of studies on the imide-amide and imide-imide rearrangements have been carried out during the last ten years.

The IPC nomenclature recommended by IUPAC [6] is used in this review, but in a number of instances, the names of compounds are quoted as given by the authors of the studies under consideration.

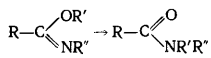
II. THE IMIDE-AMIDE REARRANGEMENT

In a general form the imide-amide rearrangement can be represented schematically as follows [7]:

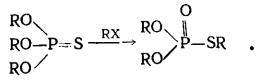


where Z-X is an electrophile and A and B are substituents at the phosphorus atom. Alkyl halides, acyl halides, phosphorus acid chlorides, chlorotrimethylsilane, or the IPC itself (in thermal isomerisation) may be used as the electrophiles. Dealkylation reactions during hydrolysis and on treatment with acids also belong to imide-amide rearrangements.

The imide-amide rearrangement of IPC may be compared with the rearrangement of alkyl imidocarboxylate esters to the corresponding amides [8]:



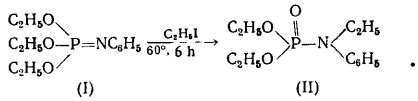
The analogy between the imide-amide rearrangement and the Pishchimuka rearrangement [9] should also be noted:



This analogy is not merely formal, being manifested also by the conditions of the rearrangement and the factors which influence its rate.

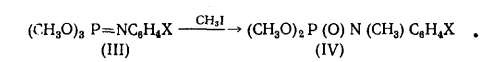
1. Rearrangement Under the Influence of Alkylating and Acylating Agents

(a) Rearrangement under the influence of alkyl halides. The first example of the imide-amide rearrangement was described by Kabachnik and Gilyarov [1] in relation to the transformation of triethyl phenylimidophosphate (I) into *O,O*-diethyl-*N*-ethylanilidophosphate (II):



(I) (II)

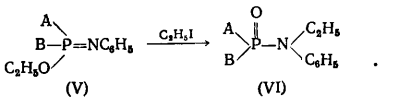
A study of the reaction of trimethyl arylimidophosphates (III) on refluxing with methyl iodide showed [10,11] that electron-accepting substituents in the benzene ring hinder the isomerisation:



(III) (IV)

The influence of alkyl halides on the rate of rearrangement of the imidophosphate (I) has been followed in relation to benzyl chloride and ethyl iodide. In the former case the rearrangement proceeds under more severe conditions (heating for 5 h at 130°C) than in the latter (refluxing for 6 h). Thus the same behaviour is observed as in the Pishchimuka thione-thiol rearrangement [12].

A number of workers [11,13,14] studied in detail the influence of substituents A and B in ethoxy(phenylimido)phosphorus compounds (V), having investigated the kinetics of their reactions with ethyl iodide in acetonitrile at 50°C:



(V) (VI)

It was found that the kinetics are described satisfactorily by a pseudo-first order equation. The rate constants are given in the Table.

The rate constants for the rearrangement of phosphorus(V) acid phenylimides $AB(C_2H_5O)P{=}NC_6H_5$ under the influence of ethyl iodide.

A	B	10^3k, litre mole^{-1} min^{-1}	A	B	10^3k, litre mole^{-1} min^{-1}
C_2H_5O	C_2H_5O	0.92	C_2H_5	C_2H_5O	3.06
C_6H_5	C_2H_5O	1.14	C_2H_5	C_6H_5	4.13
CH_3	C_2H_5O	2.85	C_2H_5	C_2H_5	10.45

It has been established[15] that the rearrangement of triphosphatriazines and tetraphosphatetrazines is catalysed by alkyl halides. Thus tetraphosphatetrazine (VII) is converted into 2,4,6,8-tetraethoxy-1,3,5,7-tetraethyl-2,4,6,8-tetraphospha-1,3,5,7-tetrazine(VIII) on heating with ethyl iodide (4.7 h, 170°C):

$$\underset{\text{(VII)}}{N_4P_4(OR)_8} \xrightarrow{RI} \underset{\text{(VIII)}}{(RO)\overline{|P(O)[N(R)P(O)(OR)]_3NR|}}\ ;\quad R=C_2H_5\ .$$

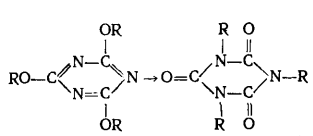
When alkyl halides were used with an alkyl group different to that in the initial triphosphatriazine (**IX**), compound (**X**), containing different substituents at the phosphorus and nitrogen atoms, was obtained[16]:

$$\underset{\text{(IX)}}{N_3P_3(OR)_6} \xrightarrow[-RX]{R'X} \underset{\text{(X)}}{(RO)\overline{|P(O)[N(R')P(O)(OR)]_2NR'|}}\ ;\quad R=C_2H_5\ .$$

When triphosphatriazine (**IX**) was refluxed with ethyl iodide in the dark for a week, it was possible to obtain the partial rearrangement product (**XI**), which, on further heating with isopropyl iodide (35 min, 175–180°C), was converted into 1,3-di-isopropyl-2,4,6-triethoxy-5-ethyl-2,4,6-triphospha-1,3,5-triazine (**XII**):

$$\text{(IX)} \xrightarrow{C_2H_5I} \underset{\text{(XI)}}{C_2H_5O\overline{|P(O)N{=}P(OC_2H_5)_2N{=}P(OC_2H_5)_2|}NC_2H_5} \xrightarrow{\text{iso-}C_3H_7I} \underset{\text{(XII)}}{C_2H_5O\overline{|P(O)N(C_3H_7\text{-iso})\text{-}P(O)(OC_2H_5)N(C_3H_7\text{-iso})P(O)(OC_2H_5)|}NC_2H_5}\ .$$

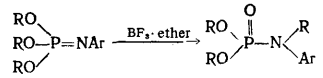
It is noteworthy that a similar rearrangement of alkyl cyanurates has been observed. Under the influence of electrophiles or on heating (180–210°C), 2,4,6-trialkoxy-1,3,5-triazines are converted into 1,3,5-trialkyl-2,4,6-trioxo-1,3,5-triazines[17] (**XIII**):



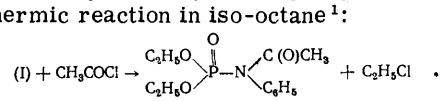
(XIII)

The synthesis of (IV) and (VI) via the imide–amide rearrangement is of preparative value[10,11,13]. A number of chromatographically pure *N*-methylanilines have been synthesised by the hydrolysis of dimethyl *N*-methylanilidophosphates.

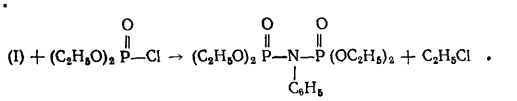
(b) Rearrangement in the presence of catalytic amounts of boron trifluoride etherate. It was found[18] that the imide–amide rearrangement of arylimidophosphorus compounds takes place under mild conditions (at room temperature or on slight heating) in the presence of catalytic amounts of boron trifluoride etherate:



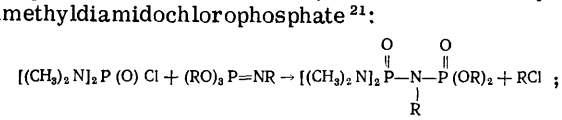
(c) Rearrangement under the influence of acyl halides, phosphorus acid chlorides, and chlorotrimethylsilane. The reactions of IPC with acylating agents take place much more vigorously than with alkyl halides. Triethyl phenylimidophosphate (I) gives rise to diethyl *N*-acetylanilidophosphate as a result of an exothermic reaction in iso-octane[1]:



The reactions of dialkyl chlorophosphates and diphenyl chlorophosphinate with phenylimido- and methylimidophosphorus compounds take place vigorously, the corresponding bisphosphoryl compounds being formed[19,20], for example:



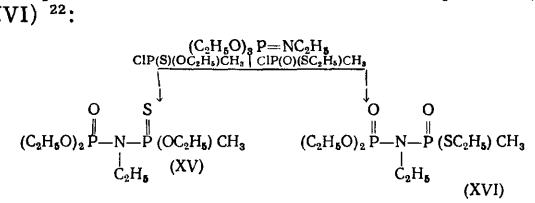
Compounds (**XIV**) have been synthesised similarly from tetramethyldiamidochlorophosphate[21]:



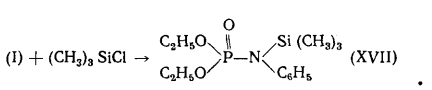
(XIV)

$R=CH_3$ or C_2H_5 .

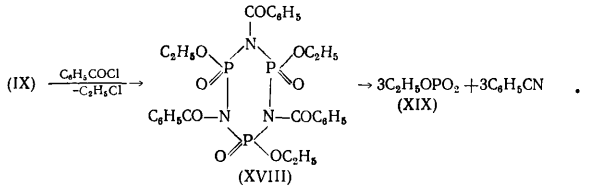
The reaction of *O*-ethyl methylchlorothiophsophonate and *S*-ethyl methylchlorothiophosphonate with triethyl ethylimidophosphate leads to the formation of compounds (**XV**) and (**XVI**)[22]:



Thus, in all the reactions of IPC with phosphorus acid chlorides considered phosphorylation takes place at the imide nitrogen atom. This reaction has been suggested as a general method of synthesis of bisphosphoryl-*N*-aryl(or alkyl)imides and (phosphoryl)(thiophosphoryl)-*N*-aryl(or alkyl)imides. Thus bis(diphenylphosphoryl)-*N*-phenylimide, obtained by the method discussed, could not be synthesised by any other procedure[23]. *N*-Trimethylsilyl derivatives of phosphoric acid amides have been obtained by the reaction of phenylimidophosphorus compounds with chlorotrimethylsilane (4 h, 50°C), for example compound (**XVII**):



The reactions of benzoyl chloride with 2,2,4,4,6,6-hexaethoxy-2,4,6-triphospha-1,3,5-triazine (**IX**) (1 h, 130–140°C) and 2,2,4,4,6,6,8,8-octaethoxy-2,4,6,8-tetraphospha-1,3,5,7-tetrazine (5 h, 140–150°C) have been investigated[15,24,25]. A mixture of products is obtained in both cases (ethyl chloride, ethyl metaphosphate, and benzonitrile). The authors suggest that the first stage of the reaction is an imide–amide rearrangement as a result of nucleophilic attack by the nitrogen atom on the carbon atom of the carbonyl group; this results in the formation of ethyl chloride and the unstable 1,3,5-tribenzoyl-2,4,6-triethoxy-2,4,6-triphospha-1,3,5-triazine (**XVIII**):



(XVIII)

The intermediate (**XVIII**) forms on decomposition ethyl metaphosphate (**XIX**) and benzonitrile. Part of the latter is converted into 2,4,6-triphenyl-1,3,5-triazine under the reaction conditions.

2. Rearrangement During Hydrolysis and on Treatment with Acids

When IPC with at least one alkoxy-group at the phosphorus atom are hydrolysed or treated with acids, they are dealkylated and the imidophosphates is converted into the amidophosphate, i.e. an imide–amide rearrangement takes place. Extensive experimental data on the hydrolysis of IPC have been surveyed in a monograph[26].

The general characteristics are in this case the same as on treatment with other electrophiles, namely the resistance to hydrolysis on treatment with acids increases with enhancement of the electron-accepting properties of the substituent at the nitrogen atom. Thus triethyl methylimidophosphate is readily hydrolysed by atmospheric moisture and on mixing with water heat is evolved[27]:

$$(C_2H_5O)_3P{=}NCH_3 \xrightarrow{H_2O} (C_2H_5O)_2P(O)NHCH_3 + C_2H_5OH \ .$$

The imidophosphate (I) is converted into diethyl anilidophosphate (**XX**) on treatment with benzoic acid in xylene at room temperature[1]:

$$(C_2H_5O)_3P{=}NC_6H_5 \begin{cases} \xrightarrow{H_2O} (C_2H_5O)_2P(O)NHC_6H_5 + C_2H_5OH \\ \qquad\qquad (XX) \\ \xrightarrow{C_6H_5COOH} (C_2H_5O)_2P(O)NHC_6H_5 + C_6H_5COOC_2H_5 \\ \qquad\qquad (XX) \qquad\qquad (XX) \end{cases} .$$

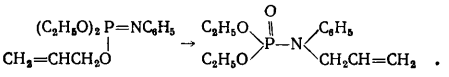
Triethyl diethoxyphosphorylimidophosphate is resistant to the action of formic or acetic acid on heating[27]. It has been found that the interaction of imidophosphates with dry hydrogen chloride is the best method for converting imidophosphates $(RO)_3P{=}NR'$ into amidophosphates $(RO_2)P(O)NHR'$, where R′ is an aryl[1,29], acetyl[30], halogenoacetyl[30], methanesulphonyl[28], dialkoxyphosphoryl, or dialkoxythiophosphoryl[31] group, for example[30]:

$$(C_2H_5O)_3P{=}NCOCF_3 \xrightarrow{HCl} (C_2H_5O)_2P(O)NHCOCF_3 + C_2H_5Cl \ .$$

3. Rearrangement on Heating (Thermal Isomerisation)

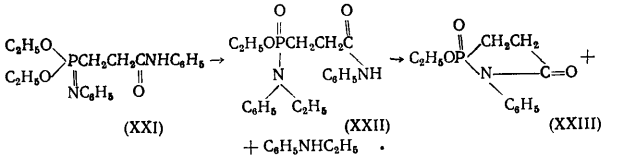
The greatest number of studies on the imide–amide rearrangement have been devoted to the thermal isomerisation of IPC. Such isomerisation was observed for the first time by Kabachnik and Gilyarov for trimethyl phenylimidophosphate[1]. On being vacuum distilled (at 150–180°, 0.1 mmHg), this substance partly isomerised to dimethyl *N*-methylanilidophosphate. It is of interest to compare this reaction with the thermal isomerisation of trimethyl thionophosphate and trimethyl thiolophosphate[32]. We shall consider the factors influencing the ease of the thermal isomerisation of IPC of the type (RO)ABP=NX; these are as follows: (a) the structure of R in the alkoxy-group; (b) the nature of the sudstituents A and B at the phosphorus atom and of the substituent X at the nitrogen atom.

The isomerisation proceeds most readily with methyl esters and is hindered as R increases in size. It has been shown[33] that thermal isomerisation of allyl diethyl phenylimidophosphate takes place at 160°C and the allyl group is the alkylating species:



It is of interest to note that the replacement of the ethoxy-groups at the phosphorus atom by the more electron-accepting phenoxy-groups facilitates isomerisation, which takes place even on distillation (90–120°C).[34]

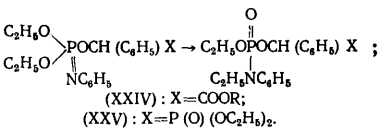
Pudovik and coworkers described a number of instances of the imide–amide rearrangement. When an attempt was made to distill the imidophosphonate (**XXI**), the cyclic phosphonate (**XXIII**) was obtained[35], evidently owing to cyclisation of the product (**XXII**) of the imide–amide rearrangement formed initially:



(XXI) (XXII) (XXIII)

$+ C_6H_5NHC_2H_5$.

The thermal isomerisation of the imidophosphates (**XXIV**)[36] and (**XXV**)[37] leads to the corresponding *N*-ethylanilidophosphates:

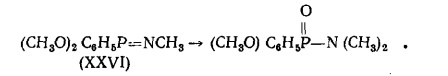


(XXIV): X=COOR;
(XXV): X=P(O)$(OC_2H_5)_2$.

It is noteworthy that the ethoxy-group is then involved in the isomerisation (when the phenyl group is present at the nitrogen atom)[35–37].

When an attempt was made to obtain trialkyl imidophosphates unsubstituted at the nitrogen atom by the interaction of trialkyl phosphites with hydrazoic acid, their thermal isomerisation products were isolated: *O,O*-dialkyl *N*-alkylamidophosphates[38,39].

When a methyl or ethyl group is present at the nitrogen atom, heat is required for the rearrangement[40]. Thus trimethyl methylimidophosphate and *O,O*-dimethyl phenyl-(methylimido)phosphonate (**XXVI**) isomerised to the corresponding amides in 1.5 h at 120°C:

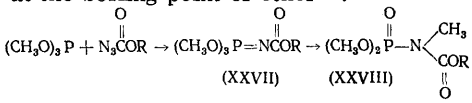


(XXVI)

It was not possible to isolate the thermal isomerisation products of ethylimidophosphorus compounds[40]. The thermal isomerisation of trimethyl methylimidophosphate has been mentioned[41], but without a description of the experiment.

A considerable number of studies have been devoted to the thermal isomerisation of IPC containing electron-accepting substituents at the nitrogen atom—such as alkoxycarbonyl (ROCO), arenesulphonyl ($ArSO_2$), disubstituted phosphoryl [XYP(O)], dialkoxythiophosphoryl [$(RO_2)P(S)$], etc. groups.

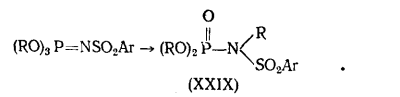
Trimethyl alkoxycarbonylimidophosphates (XXVII) isomerise at the boiling point of ether [42]:



(XXVII) (XXVIII)

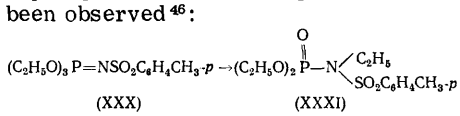
This results in the formation of the corresponding dimethyl *N*-alkoxycarbonylmethylamidophosphates (XXVIII). The replacement of the methoxy-group at the phosphorus atom in compound (XXVII) by electron-donating substituents (a methyl group [43] or a dimethylamino-group [44]) increases the resistance to thermal isomerisation; the corresponding compounds may be vacuum distilled without decomposition.

It has been shown [45] that trialkyl arenesulphonylimidophosphates isomerise on heating to esters of *N*-arenesulphonyl-*N*-arylamidophosphoric acids (XXIX):



(XXIX)

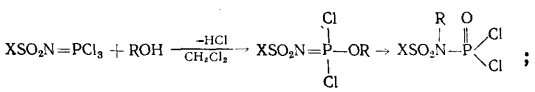
The isomerisation of triethyl toluene-*p*-sulphonylimidophosphate (XXX) to diethyl *N*-toluene-*p*-sulphonyl-*N*-ethylamidophosphate (XXXI) during distillation (at 200°C) has been observed [46]:



(XXX) (XXXI)

According to the authors [46], (XXXI) is partly converted into the initial imidophosphate (XXX) at 200°C, i.e. the reversible reaction (XXX) ⇌ (XXXI) takes place. However, the evidence which they present (changes in the ^1H NMR spectrum) is insufficient to sustain this claim.

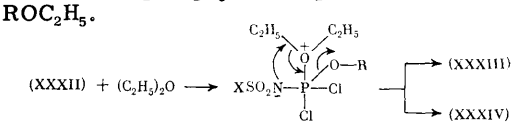
The imide–amide rearrangement of *O*-alkyl dichloro-(halogenosulphonylimido)-phosphates (XXXII) to amidophosphates (XXXIII) under the influence of ether or dioxan has been observed [47,48]:



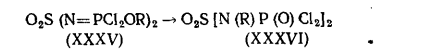
(XXXII) (XXXIII)

R=CH_3, C_2H_5, or iso-C_3H_7, X=Cl, or F.

The imidophosphates (XXXII) cannot be vacuum distilled (decomposition) and, on refluxing them in ether (or dioxan) for 20 min, compounds (XXXIII) were obtained in high yields. Together with the main product (XXXIII), the catalytic isomerisation results in the formation of the *N*-ethylamide $XSO_2N(C_2H_5)P(O)Cl_2$ (XXXIV) and the mixed ether ROC_2H_5.



The authors [49] observed that, when *NN*-bis(alkoxydichlorophosphoranylidene)-sulphamides (XXXV) isomerise, the alkyl group also migrates to the nitrogen atom with formation of the amidophosphates (XXXVI):

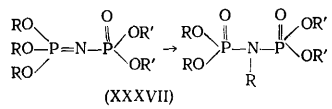


(XXXV) (XXXVI)

The authors [49] noted that ether influences the rate of isomerisation. The phenyl ester (XXXV, R = C_6H_5) does not isomerise even on prolonged heating.

The mode of thermal isomerisation of phosphoryl-imidophosphates $(RO)_3P{=}NP(O)XY$ depends on the nature of the substituents at the phosphorus atom (X and Y). When X and Y are alkoxy-groups, the alkyl group migrates exclusively to the imide nitrogen atom. When X and Y are electron-donating (alkyl) groups, the oxygen atom of the phosphoryl group is alkylated (imide–imide rearrangement). If X is an alkyl and Y an alkoxy-group, there is a possibility of the formation of products of both imide–amide and imide–imide rearrangements.

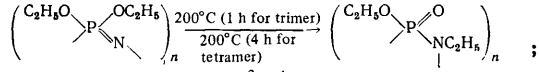
The rate of thermal isomerisation of trialkyldialkoxy-phosphorylimidophosphates (XXXVII) depends markedly on the nature of the alkyl substituent R [50]:



(XXXVII)

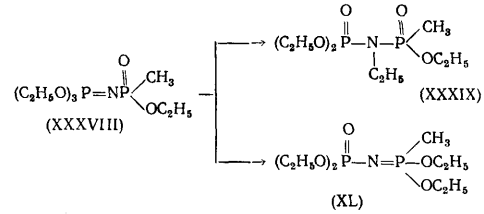
Thus trimethyl dimethoxyphosphorylimidophosphate $(CH_3O)_3P{=}NP(O)(OCH_3)_2$ partly isomerises at 50–60°C, and on vacuum distillation (100°C) the isomerisation goes to completion; triethyl dimethoxyphosphorylimidophosphate $(C_2H_5O)_3P{=}NP(O)(OCH_3)_2$ isomerises only as a result of heating for many hours at 150–160°C.

The thermal isomerisation of 2,2,4,4,6,6-hexaethoxy-2,4,6-triphospha-1,3,5-triazine, 2,2,4,4,6,6,8,8-octaethoxy-2,4,6,8-tetraphospha-1,3,5,7-tetrazine, [15,51] and 2,2,4,4,6,6,8,8-octa-(β-chloroethoxy)-2,4,6,8-tetraphospha-1,3,5,7-tetrazine (refluxing for 16 h in dichloroethane) [52] also leads to *N*-alkyl derivatives:



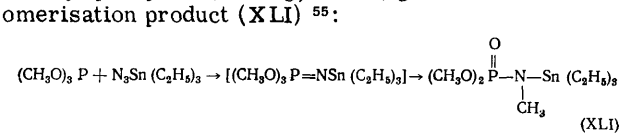
n = 3 or 4.

Two products are formed from triethyl ethoxymethylphosphorylimidophosphate (XXXVIII): the product of the imide–amide rearrangement (XXXIX) under more severe conditions (at 170°C) and the product of the imide–imide rearrangement (XL) under milder conditions (at 130°C) [53,54]:



(XXXVIII) (XXXIX) (XL)

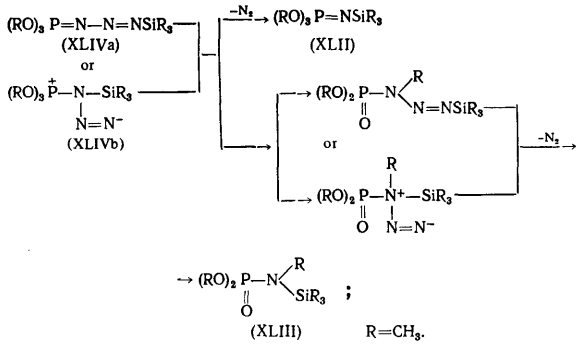
The imide–imide rearrangement of compounds containing other substituents at the nitrogen atom has been little investigated. The reaction of triethylstannyl azide with trimethyl phosphite (heating, 160°C) gave the thermal isomerisation product (XLI) [55]:



(XLI)

When trimethyl phosphite interacts with trimethylsilyl azide (8 h, 100–120°C), dimethyl *N*-methyl-*N*-trimethylsilylamidophosphate (XLIII) is formed together with trimethyl trimethylsilylimidophosphate (XLII). [56] Since the imidophosphate (XLII) is stable on heating (4 h, 190–200°C), the authors [56] suggested that the intermediate of Staudinger's reaction (cf. Ref. 57), namely the triazene

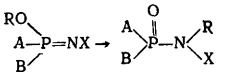
(XLIVa) or the betaine (XLIVb), undergoes the imide–amide rearrangement:



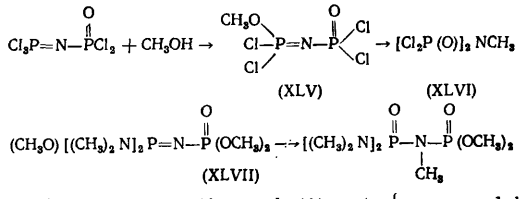
(XLIII) R=CH_3.

It has been shown recently[58] that, when the imidophosphate $(CF_3CH_2O)_3P{=}NSi(CH_3)_3$ is heated to 200°C, the imide–amide rearrangement does not occur and the linear polymeric product $[-N{=}P(OCH_2CF_3)_2-]_n$ is formed.

Examination of studies on the imide–amide rearrangement on heating permits a conclusion concerning the influence of the substituents at the phosphorus and nitrogen atoms on the rate of isomerisation:



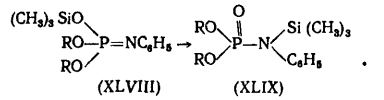
Since the IPC itself plays the role of the alkylating agent in thermal isomerisation, enhancement of the electron-accepting properties of substituents A and B facilitates the isomerisation. Thus *O*-methyl dichloro(dichlorophosphorylimido)phosphate (XLV) partly isomerises to bis(dichlorophosphoryl)-*N*-methylimide (XLVI)[59] even at room temperature. On the other hand, *O*-methyl *N*,*N*,*N*′,*N*′-tetramethyldiamido(dimethoxyphosphorylimido)phosphate (XLVII) remains unchanged after heating for 10 h at 95–100°C, decomposing under more severe conditions (5 h, 130°C)[21]:



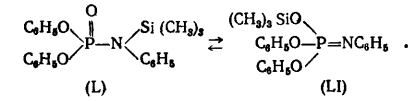
When electron-accepting substituents {arenesulphonyl ($ArSO_2$), dialkoxyphosphoryl [$(RO)_2P(O)$], and similar groups} are introduced at the nitrogen atom, the alkylation capacity of the IPC increases sharply and the thermal isomerisation is facilitated despite the fact that the electron-accepting substituents at the nitrogen atom make the IPC much less nucleophilic. The alkylating capacity of IPC with powerful electron-accepting substituents at the nitrogen atom is greatly superior to that of the corresponding phosphates and thiophosphates[4,7,10].

4. Rearrangement with Participation of the Trimethylsilyl Group

In the examples considered hitherto, the imide–amide rearrangement was irreversible with the exception of the rearrangement of compound (XXXI),[46] which we believe requires confirmation. Instances of both irreversible and reversible migration of the trimethylsilyl group in the $(CH_3)_3Si{-}O{-}P{=}N{-}$ system have been discovered in recent years. The irreversible migration has been found in phosphazines[60]. It has been shown that phosphazines, formed as intermediates in the reaction of dialkyl trimethylsilyl phosphites with methyl diazoacetate, isomerise completely to the corresponding dialkyl *N*-methoxycarbonylmethylene-*N*′-trimethylsilylhydrazidophosphates $(RO)_2P(O)N[Si(CH_3)_3]N{=}CHCOOCH_3$ even at room temperature. Dialkyl trimethylsilyl phenylimidophosphates (XLVIII), formed in the reaction of dialkyltrimethylsilyl phosphites with phenyl azide, are converted under the reaction conditions into dialkyl *N*-phenyl-*N*-trimethylsilylamidophosphates (XLIX).[61,62]



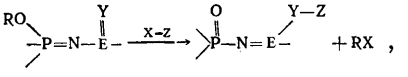
The reversible migration of the trimethylsilyl group in the O–P=N–system has been observed for compound (XLIX, R = CH_3) (on heating) and for diphenyl *N*-phenyl-*N*-trimethylsilylamidophosphate (L).[63] In the latter case the product contains 89% of (L) and 11% of form (LI) at 28°C:



At 129°C the contents of forms (L) and (LI) are 80 and 20% respectively (^1H and ^{31}P NMR data).

III. THE IMIDE–IMIDE REARRANGEMENT

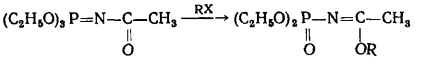
In the general case the imide–imide rearrangement can be represented schematically as follows:



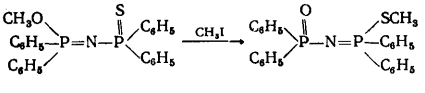
where E = C or P, Y = O or S, and X–Z are electrophiles.

1. Rearrangement Under the Influence of Alkylating and Acylating Agents

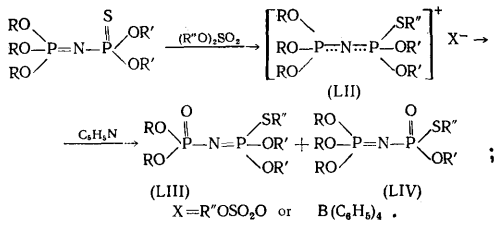
The first example of the imide–imide rearrangement was observed by Kabachnik et al.[2] on heating triethyl acetylimidophosphate with alkyl halides (100–130°C, 4–6 h). This results in the formation of *O*-alkyl *N*-(diethoxyphosphoryl)iminoacetates, i.e. the rearrangement proceeds at the carbonyl oxygen atom:



Thiophosphorylimidophosphates are alkylated usually at the thiono-sulphur atom. The reaction of *O*-methyl diphenyl(diphenylthiophosphorylimido)phosphinate with methyl iodide has been described[64]:



Khodak, Gilyarov, and Kabachnik[65,66] showed that the reaction of trialkyl dialkoxythiophosphorylimidophosphates with dialkyl sulphates proceeds via a stage involving the formation of quasi-phosphonium salts (LII), which decompose under the influence of nucleophiles with formation of the products of the imide–imide [compound (LIII)] and (or) thione–thiol [compound (LIV)] rearrangements:

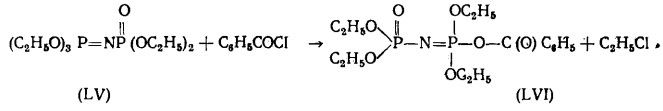


(LII)

(LIII) (LIV)

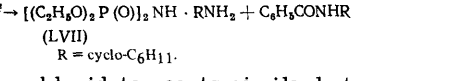
X = $R''OSO_2O$ or $B(C_6H_5)_4$.

The imide–imide rearrangement proceeds via the reaction of phosphorylimidophosphates with acylating agents. Thus in the reaction of triethyl diethoxyphosphorylimidophosphate (LV) with benzoyl chloride (10 h, 60°C) the acylation is directed to the phosphoryl oxygen atom and the anhydride (LVI) is formed, its structure being confirmed by ^{31}P NMR:



(LV) (LVI)

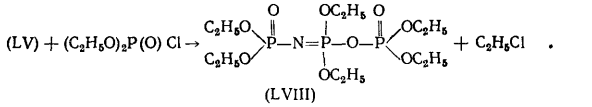
The presence of the anhydride linkage has been demonstrated by the reaction with cyclohexylamine from which cyclohexylbenzamide and the cyclohexylammonium salt of bis(diethoxyphosphoryl)imide (LVII) were isolated[18,67]:



(LVII)

R = cyclo-C_6H_{11}.

Diethyl phosphorochloridate reacts similarly to benzoyl chloride:

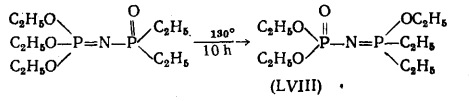


(LVIII)

O-Ethyl *N,N,N',N'*-tetraethyldiamido(diethoxyphosphorylimido)phosphate $C_2H_5O[(C_2H_5)_2N]_2P{=}NP(O)(OC_2H_5)_2$ reacts with benzoyl chloride and diethyl phosphorochloridate similarly to the imidophosphate (LV).[18,67]

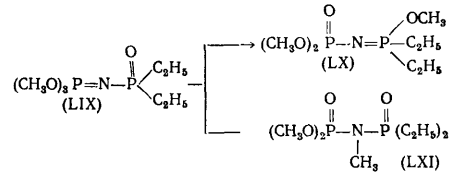
2. Thermal Isomerisation

The imide–imide rearrangement of phosphorylimidophosphates was observed for the first time[3] in the thermal isomerisation of triethyl diethylphosphorylimidophosphate and has been called by the authors the "phosphazene–phosphoxide rearrangement":



(LVIII) .

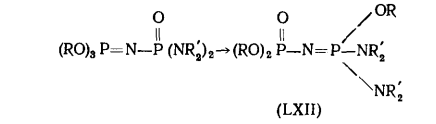
As shown in subsequent studies[53,68], the imide–imide rearrangement of phosphorylimidophosphates $(RO)_3P{=}NP(O)XY$ (X and Y are alkyl or phenyl groups) is of a general type. It proceeds readily for methoxy-derivatives. Thus even at 20°C trimethyl diethylphosphorylimidophosphate (LIX) undergoes partial isomerisation after a few days, and virtually complete isomerisation after four months, to the ester (LX); the product of the imide–amide rearrangement (LXI) is also formed as an admixture:



(LIX) (LX) (LXI) .

On thermal isomerisation, trialkyl alkoxyalkylphosphorylimidophosphates give rise to products of the imide–amide or imide–imide rearrangement, depending on the reaction conditions[54,69] (see Section II, subsection 3).

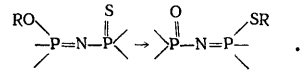
The imide–imide rearrangement with formation of the imidophosphates (LXII) is observed in the thermal isomerisation of trialkyl tetra-alkyldiamidophosphorylimidophosphates, the rate of isomerisation decreasing in the following sequence of groups R : $CH_3 > C_2H_5 > C_4H_9$:



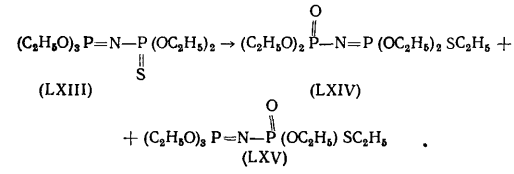
(LXII)

For example, trimethyl tetraethyldiamidophosphorylimidophosphate isomerises in 6 h at 85–90°C.[21]

In the thermal isomerisation of thiophosphorylimidophosphates mainly the thiono-sulphur atom is attacked, i.e. the imide–imide rearrangement takes place:



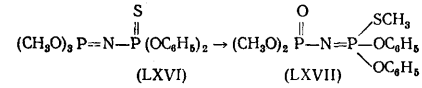
When triethyl diethoxythiophosphorylimidophosphate (LXIII) is heated (6 h, 140°C), the imidophosphates (LXIV) and (LXV) are formed[4,7]:



(LXIII) (LXIV)

(LXV) .

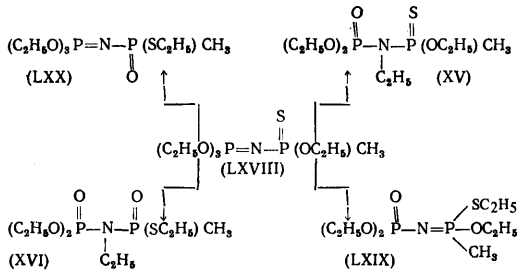
Attack on the sulphur atom occurs in the thermal isomerisation of trimethyl diphenoxythiophosphorylimidophosphate (LXVI) to the imidophosphate (LXVII)[70]:



(LXVI) (LXVII) .

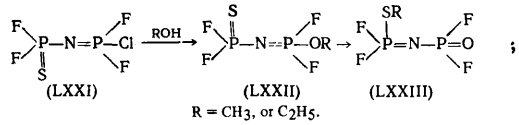
The thermal isomerisation of triethyl ethoxymethylthiophosphorylimidophosphate (LXVIII) (130°C, 10–11 h) takes place in a much more complex manner. A detailed study of this reaction[22] showed that, together with the main product *O*-ethyl *S*-ethyl (diethoxyphosphorylimido)methylphosphonate (LXIX) (77.4%), the isomers (XV), (LXX),

and (**XVI**) are formed in small amounts (8.5, 10.4, and 3.7% respectively; GLC data):

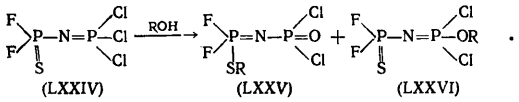


According to earlier results[71], the thermal isomerisation of the imidophosphate (**LXVIII**) yields only (**XV**) under these conditions.

The introduction of a halogen atom at the phosphorus atom joined to the imide group in thiophosphorylimidophosphates increases sharply the rate of isomerisation. When difluorothiophosphorylimidophosphorus chloride difluoride (**LXXI**) reacts with methanol or ethanol[72,73], the resulting esters (**LXXII**) isomerise to the thioesters (**LXXIII**) already during the reaction:

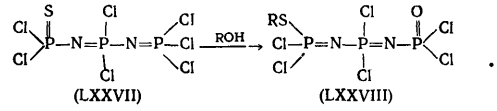


Such isomerisation is difficult for the products of the reaction of difluorothiophosphorylimidophosphorus trichloride (**LXXIV**) with alcohols:



Thus the decrease of the electronegativity of the substituents at the phosphorus atom joined to the imide group (on passing from fluorine to chlorine) hinders the isomerisation.

The *S*-isomers (**LXXVIII**) were isolated in the reaction between (**LXXVII**) and methanol or ethanol (at 20°C) [75]:

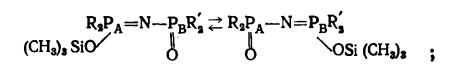


Consequently the removal of the alkylating group RO to the ($-N=PCl_2-$) fragment does not affect the ease of isomerisation.

3. Rearrangement with Participation of the Trimethylsilyl Group

In all the instances considered hitherto the imide–imide rearrangement was irreversible.

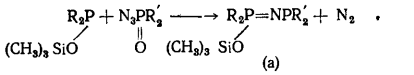
It has been found[62,76] by $^{31}P-\{^1H\}$ NMR that the trimethylsilyl group in many phosphorylimidophosphates [(**LXXIX**)–(**LXXXIV**)] undergoes both reversible [(a)⇌(b)] and irreversible [(a) → (b)] transfers:



(**LXXIX**): R=R′=OCH_3; (**LXXX**): R=R′=OC_2H_5;
(**LXXXI**): R=OC_2H_5, R′=OC_4H_9-iso; (**LXXXII**): R′=OC_2H_5,
R′=N$(CH_3)_2$; (**LXXXIII**): R=OC_2H_5, R′=C_2H_5;
(**LXXXIV**): R=OCH_3, R′=OC_2H_5.

A reversible transfer of the trimethylsilyl group has been observed for the imidophosphates (**LXXIX**)–(**LXXXI**) (the spectrum contains one broad signal at room temperature and an AB-quartet due to the two non-equivalent phosphorus atoms appears at a reduced temperature where exchange is inhibited). The observed changes in the spectrum as a function of temperature indicate the occurrence of slow (in terms of the NMR time scale) exchange. This made it possible to determine the lifetime τ of each isomeric form.

An irreversible transfer of the trimethylsilyl group has been observed for the imidophosphates (**LXXII**)–(**LXXXIV**). On the basis of the scheme used for the synthesis, compounds (a) should have been formed in the absence of a rearrangement:



However, in fact the compounds obtained have a structure corresponding to form (b) according to $^{31}P-\{^1H\}$ NMR spectra, i.e. under the reaction conditions the trimethylsilyl group passes to the phosphoryl oxygen linked to the P_B atom.

Later Riesel and coworkers[77,78] reported the reversible migration of the trimethylsilyl group in the "symmetrical" imidophosphates $[(CH_3)_3SiO]R_2P{=}NP(O)PR_2$ (R is an alkoxy or a dialkylamido-group) on the basis of ^{31}P NMR spectra.

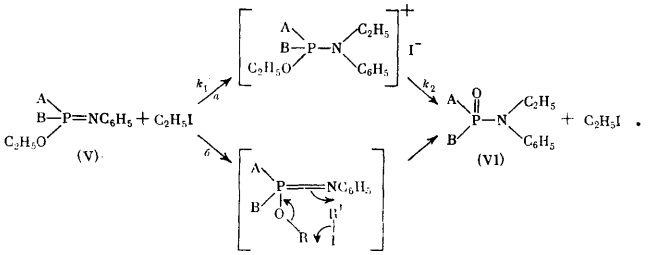
The reversible migration of other groups (ethyl, benzoyl, or benzyl) in the imidophosphates $R_2(XO)P{=}NP.(O)R_2$ [R = OC_2H_5, X = C_2H_5 or C_6H_5CO; R = $N(C_2H_5)_2$, X = $C_6H_5CH_2$] could not be observed at temperatures between −80°C and +90°C according to $^{31}P-\{^1H\}$ NMR data[76].

IV. THE MECHANISMS OF THE IMIDE–AMIDE AND IMIDE–IMIDE REARRANGEMENTS

There have been few studies devoted to the investigation of the mechanisms of the above rearrangements. In some cases only hypotheses concerning the mechanism have been put forward.

As stated above, the kinetics of the reaction of ethoxy(phenylimido)phosphorus compounds (V) with ethyl iodide have been studied[11,13,14]. Two alternative pathways had been suggested previously to account for the mechanism of the imide–amide rearrangement[1]: (a) a two-stage

pathway with an intermediate quasi-phosphonium compound (b) a single-stage pathway with a cyclic transition stage:

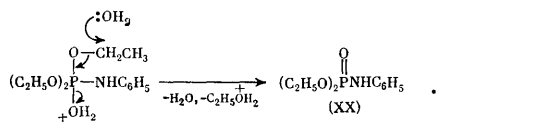


The logarithms of the rate constants listed in the Table are linearly correlated with σ^{ph} for the substituents at the phosphorus atom:

$$\lg k = 3.44 - 0.604 \sum \sigma^{ph} .$$

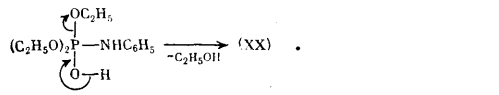
The low absolute value of the correlation parameter $\rho = 0.604$ supports a cyclic transition state, i.e. mechanism (b).

The study of the mechanism of the hydrolysis of triethyl phenylimidophosphate (I) in the presence of $H_2^{18}O$ at different pH (between 2 and 8) showed[79] that the content of ^{18}O in the hydrolysis products depends on pH [from 22% at low pH values (pH ~ 2) to 80% at high pH values (pH ~ 8)]. The authors[79] suggest that at low pH values the adduct of the protonated imidophosphate and water is dealkylated under the influence of another water molecule with elimination of the water molecule which had added on initially:



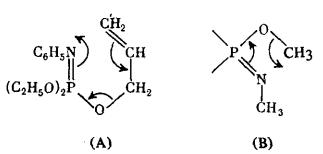
Under these conditions, all the oxygen atoms in the imidophosphate (I) are retained in the amidophosphate (**XX**).

At higher pH values the neutral form of the intermediate may decompose with expulsion of the ethoxy-group:



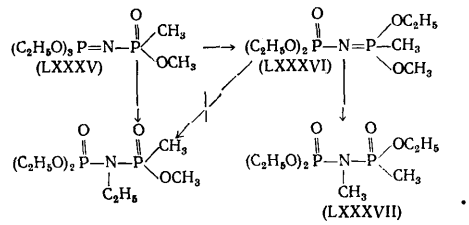
It is suggested that this entails an increase of the content of labelled oxygen in the amide (**XX**) formed.

The mechanism of the thermal isomerisation of aryl or alkyl imidophosphates has not been specially studied. Pudovik and coworkers[33,34] investigated the thermal isomerisation of *O*-allyl phenylimidophosphates and concluded that it is an intramolecular process with a cyclic transition state (A) (the reaction is accompanied by the inversion of the allyl group). Referring to these results, Goldwhite et al.[40] suggested that the thermal isomerisation of trimethyl methylimidophosphate also proceeds via the intramolecular mechanism (B):



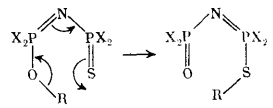
(A) (B)

A study of the isomerisation of triethyl methoxymethylphosphorylimidophosphate (**LXXXV**) by ^1H NMR showed[69] that an imide–imide rearrangement takes place initially with formation of the imidophosphate (**LXXXVI**) and then, after further heating, it is followed by an imide–amide rearrangement; the methyl group then migrates to the nitrogen atom and compound (**LXXXVII**) is formed:



As regards the mechanism of the imide–imide rearrangement of phosphorylimidophosphates, it has been suggested that the reaction is intermolecular in the case of trialkyl dialkylphosphorylimidophosphates[68] or triethyl methoxymethylphosphorylimidophosphate (**LXXXV**).[69]

It has been suggested[74] that the conversion of *O*-alkyl dihalogeno(dihalogenothiophosphorylimido)phosphates into the *S*-alkyl isomers is likewise an intramolecular process and can be represented schematically as follows:

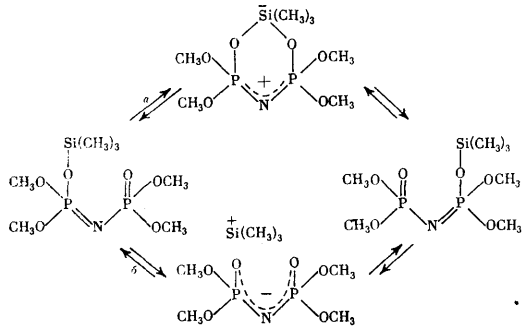


Khodak et al.[70] studied the mechanism of the imide–imide rearrangement in relation to the thermal isomerisation of trimethyl diphenoxythiophosphorylimidophosphate (**LXVI**). The kinetics of the isomerisation at 98°C in bromobenzene are described satisfactorily by a second-order equation [$k = (6.3 \pm 0.3) \times 10^{-5}$ litre mole^{-1} s^{-1}]. Having investigated the influence of temperature and the dielectric constant of the medium on the isomerisation rate constant, the authors[70] concluded that the mechanism involving intermolecular alkylation with a low-polarity transition state and the formation of an ion pair as a rapidly reacting intermediate is most probable for the isomerisation of the imidophosphate (**LXVI**) to the imidophosphate (**LXVII**):



In order to elucidate the mechanism of the migration of the trimethylsilyl group (see above), the order of the reaction of dimethyl trimethylsilyl dimethoxyphosphorylimidophosphate (**LXXIX**) was determined. The dependence of the lifetime of one of the tautomeric forms [the lifetimes are the same for the imidophosphate (**LXXIX**)] on concentration was investigated by ^1H NMR.[76] It was found that at the same temperature the lifetimes are the same in solutions at different concentrations (in chloroform). This shows that the reaction is of first order, i.e. that the imidophosphate (**LXXIX**) undergoes an intramolecular rearrangement. Mechanism *a* involving the formation of a cyclic intermediate, may be proposed for the rearrangement, in view of the presence of the unshared *d* orbitals of the silicon atom. Nor can one rule out the

ionic mechanism *b*—the migration of the trimethylsilyl group as a cation:



Examination of the data for the imide–amide and imide–imide rearrangement permits the conclusion that the IPC containing the R–O–P=N–, R–O–P=N–P=O, and R–O–P=N–P=S groups are highly reactive.

In many instances these rearrangements may be used as a method for the synthesis of new IPC and phosphorus acid amides.

The results of the study of the thermal isomerisation permit the conclusion that, owing to the high lability of the IPC, their synthesis in a pure form requires special checks (by thin-layer chromatography, infrared spectroscopy, ^{31}P NMR, and ^{1}H NMR).

Since certain types of IPC may have practical applications as drugs[90], herbicides[81,82], and defoliants[83], the importance of studies on the imide–amide and imide–imide rearrangements can be readily understood. This field of the IPC chemistry is developing vigorously; we may expect that it will yield new interesting theoretical and practical results.

REFERENCES

1. M. I. Kabachnik and V. A. Gilyarov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 790 (1956).
2. M. I. Kabachnik, V. A. Gilyarov, and C. T. Chiang, Izv. Akad. Nauk SSSR, Ser. Khim., 665 (1965).
3. I. M. Filatova, E. L. Zaitseva, and A. Ya. Yakubovich, Zhur. Obshch. Khim., 36, 1861 (1966).
4. A. A. Khodak, V. A. Gilyarov, and M. I. Kabachnik, Zhur. Obshch. Khim., 44, 256 (1974).
5. V. A. Gilyarov and M. I. Kabachnik, Zhur. Obshch. Khim., 42, 2148 (1972).
6. International Union of Pure and Applied Chemistry, Information Bulletin, Nomenclature of Organic Chemistry: Section D, 1973, p. 75, p. 82.
7. V. A. Gilyarov, "Trudy V Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Proceedings of the Vth Conference on the Chemistry and Applications of Organophosphorus Compounds), Izd. Nauka, Moscow, 1974, p. 243.
8. B. C. Challis and A. D. Frenkel, Chem. Comm., 303 (1972).
9. P. S. Pishchimuka, Zhur. Russ. Khim. Obshch., 44, 1471 (1912).
10. V. A. Gilyarov, R. V. Kudryavtsev, and M. I. Kabachnik, Zhur. Obshch. Khim., 36, 708 (1966).
11. V. A. Gilyarov and R. V. Kudryavtsev, "Trudy IV Konferentsii po Khimii i Primeneniyu Fosfororganicheskikh Soedinenii" (Proceedings of the IVth Conference on the Chemistry and Applications of Organophosphorus Compounds), Izd. Nauka, Moscow, 1972, p. 180.
12. A. J. Burn, J. I. G. Cadogan, and A. B. Foster, Chem. Ind. (London), 591, 5532 (1961).
13. G. K. Genkina, V. A. Gilyarov, E. I. Matrosov, and M. I. Kabachnik, Zhur. Obshch. Khim., 40, 1496 (1970).
14. V. A. Gilyarov, "Symposium of Inorganic Phosphorus Compounds, Abstracts, Prague, 1970", p. 13.
15. B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, J. Chem. Soc., 4459 (1964).
16. B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, J. Chem. Soc., 7432 (1965).
17. G. F. Reynolds, R. A. Larson, and J. A. C. Allison, Mich. Acad., 4(3), 345 (1972).
18. V. A. Gilyarov, A. A. Khodak, and N. N. Zaslavskaja, "IInd Symposium on Inorganic Phosphorus Compounds, Abstracts, Prague, 1974", p. 64.
19. V. A. Gilyarov and M. I. Kabachnik, USSR P.242 166 (1968); Byul. Izobret., No. 15, 24 (1969).
20. V. A. Gilyarov, N. A. Tikhonina, and M. I. Kabachnik, Zhur. Obshch. Khim., 41, 2365 (1971).
21. N. N. Zaslavskaya, V. A. Gilyarov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 675 (1976).
22. A. A. Khodak, V. A. Gilyarov, T. M. Shcherbina, and M. I. Kabachnik, Zhur. Obshch. Khim., 46, 2482 (1976).
23. B. A. Arbuzov, N. I. Alimov, M. A. Zvereva, I. D. Neklesova, and M. I. Kudrina, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1047 (1954).
24. B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, Proc. Chem. Soc., 340 (1962).
25. B. W. Fitzsimmons, C. Hewlett, and R. A. Shaw, J. Chem. Soc., 4799 (1965).
26. G. I. Derkach, N. I. Zhmurova, A. V. Kirsanov, V. I. Shevchenko, and A. S. Shtepanek, "Fosfazosoedineniya" (Phosphazo-Compounds), Izd. Naukova Dumka, Kiev, 1965.
27. M. I. Kabachnik, V. A. Gilyarov, and E. N. Tsvetkov, Izd. Akad. Nauk SSSR, Otd. Khim. Nauk, 2135 (1959).
28. M. I. Kabachnik and V. A. Gilyarov, Izd. Akad. Nauk SSSR, Otd. Khim. Nauk, 819 (1961).
29. V. A. Gilyarov and M. I. Kabachnik, Zhur. Obshch. Khim., 36, 282 (1966).
30. M. I. Kabachnik, V. A. Gilyarov, Chen-Te Chang, and E. I. Matrosov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1589 (1962).
31. V. A. Gilyarov, E. N. Tsvetkov, and M. I. Kabachnik, Zhur. Obshch. Khim., 36, 274 (1966).
32. W. G. Emmet and H. D. Jones, J. Chem. Soc., 99, 715 (1911).
33. A. N. Pudovik, I. M. Aladzheva, and V. G. Kotova, Zhur. Obshch. Khim., 37, 1173 (1967).
34. A. N. Pudovik, I. M. Aladzheva, V. G. Kotova, and A. F. Zinkovskii, Zhur. Obshch. Khim., 39, 1528 (1969).
35. A. N. Pudovik, E. S. Batyeva, and N. V. Yastremskaya, Zhur. Obshch. Khim., 43, 437 (1973).
36. A. N. Pudovik, I. V. Konovalova, and V. P. Kakurina, Zhur. Obshch. Khim., 32, 333 (1972).
37. A. N. Pudovik, E. S. Batyeva, V. D. Nesterenko, and N. P. Anoshina, Zhur. Obshch. Khim., 44, 1674 (1974).

38. V.A.Gilyarov, "VIII Mendelevskii S'ezd po Obshchei i Prikladnoi Khimii, Sektsiya Organicheskoi Khimii" (The VIIIth Mendeleev Congress on General and Applied Chemistry. The Organic Chemistry Section), Izd.Akad.Nauk SSSR, Moscow, 1959, p.397.
39. M.I.Kabachnik and V.A.Gilyarov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 816 (1961).
40. H.Goldwhite, P.Gysegem, S.Show, and C.Swyke, J.Chem.Soc., Dalton Trans., 12 (1975).
41. P.Haaseman and J.Goubeau, Z.anorg.Chem., 408, 302 (1974).
42. V.A.Shokol, N.K.Mikhailyuchenko, and G.I.Derkach, Zhur.Obshch.Khim., 38, 337 (1968).
43. V.A.Shokol, L.I.Molyavko, and G.I.Derkach, Zhur. Obshch.Khim., 40, 998 (1970).
44. V.A.Shokol, L.I.Molyavko, and G.I.Derkach, Zhur. Obshch.Khim., 41, 2379 (1971).
45. V.I.Shevchenko, V.P.Tkach, and A.V.Kirsanov, Zhur.Obshch.Khim., 35, 1224 (1965).
46. J.T.Kay and B.K.Snell, Tetrahedron Letters, 2551 (1967).
47. H.W.Roesky and W.G.Böwing, Angew.Chem., 83, 365 (1971).
48. H.W.Roesky and W.G.Böwing, Chem.Ber., 104, 3204 (1971).
49. G.Schöning, U.Klingebiel, and O.Glemser, Chem. Ber., 107, 3756 (1974).
50. V.A.Shokol, N.K.Mikhailyuchenko, and G.I.Derkach, in "Khimiya Organicheskikh Soedinenii Fosfora" (The Chemistry of Organic Compounds of Phosphorus), Izd.Nauka, Leningrad, 1967, p.78.
51. B.W.Fitzsimmons and R.A.Shaw, Proc.Chem.Soc., 258 (1961).
52. D.F.Lawson, J.Org.Chem., 39, 3357 (1974).
53. I.M.Filatova, E.L.Zaitseva, A.N.Simonov, and A.Ya.Yakubovich, Zhur.Obshch.Khim., 38, 1304 (1968).
54. V.A.Shokol, G.A.Golik, V.T.Tsiba, Yu.P.Egorov, and G.I.Derkach, Zhur.Obshch.Khim., 40, 1680 (1970).
55. J.Lorbert, H.Kraft, and H.Nöth, Chem.Ber., 100, 3511 (1967).
56. O.Schlak, W.Stadelmann, O.Stelzer, and R.Schmutzler, Z.anorg.Chem., 419, 275 (1976).
57. H.Staudinger and J.Meyer, Helv.Chim.Acta, 2, 635 (1919).
58. E.P.Flindt, H.Rose, and H.C.Marsmann, Z.anorg.Chem., 430, 155 (1977).
59. L.Riesel, M.Willfahrt, W.Grosse, P.Kindscher-owsky, A.A.Shodak, V.A.Gilyarov, and M.I.Kabatschnik, Z.anorg.Chem., 435, 61 (1977).
60. A.N.Pudovik and R.D.Gareev, Zhur.Obshch.Khim., 45, 236 (1975).
61. L.V.Nesterov, N.E.Krepysheva, and and R.A.Sapirova, Izv.Akad.Nauk SSSR, Ser.Khim., 1908 (1975).
62. M.I.Kabachnik, N.N.Zaslavskaya, V.A.Gilyarov, P.V.Petrovskii, and V.A.Skoren', Dokl.Akad.Nauk SSSR, 228, 849 (1976).
63. R.K.G.Hodgston, R.Katz, and G.Son, J.Organo-metal.Chem., 117, C63 (1976).
64. A.Schmidpeter and H.Groeger, Chem.Ber., 100, 3979 (1967).
65. A.A.Khodak, V.A.Gilyarov, and M.I.Kabachnik, Zhur.Obshch.Khim., 45, 262 (1975).
66. A.A.Khodak, V.A.Gilyarov, and M.I.Kabachnik, Zhur.Obshch.Khim., 46, 1672 (1976).
67. N.N.Zaslavskaya, V.A.Gilyarov, and M.I.Kabachnik, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd.Nauka, Leningrad, 1976, p.84.
68. A.Ya.Yakubovich, I.M.Filatova, E.L.Zaitseva, and V.V.Sheluchenko, "Trudy IV Konferentsii po Khimii i Primeneniyu Fosforoorganicheskikh Soedinenii" (Proceedings of the IVth Conference on the Chemistry and Applications of Organophosphorus Compounds), Izd.Nauka, Moscow, 1972, p.174.
69. V.A.Schokol, "IInd Symposium on Inorganic Phosphorus Compounds, Abstracts, Prague, 1974", p.141.
70. A.A.Khodak, V.A.Gilyarov, and M.I.Kabachnik, Zhur.Obshch.Khim., 47, 273 (1977).
71. V.A.Shokol, Doctoral Thesis, Institute of General Chemistry, Academy of Sciences of Ukrainian SSR, Kiev, 1973.
72. H.W.Roesky and L.F.Grimm, Chem.Comm., 998 (1971).
73. H.W.Roesky, W.Grosse, and W.G.Böwing, Z.anorg. Chem., 386, 191 (1971).
74. H.W.Roesky, B.H.Kuhtz, and L.F.Grimm, Z.anorg. Chem., 389, 167 (1972).
75. H.W.Roesky, Z.Naturforsch., 27b, 1569 (1972).
76. N.N.Zaslavskaya and V.A.Gilyarov, "Yubileinaya Konferentsiya po Khimii Fosfororganicheskikh Soedinenii, Posvyashchennaya Stoletiyu so Dnya Rozhdeniya Akademika A.E.Arbuzova, Tezisy Dokladov" (The Jubilee Conference on the Chemistry of Organophosphorus Compounds Commemorating the Hundredth Anniversary of the Birthday of Academician A.E.Arbuzov, Abstracts of Reports), Kiev, 1977, p.37.
77. L.Riesel, A.Claussnitzer, and C.Ruby, Z.anorg. Chem., 433, 200 (1977).
78. L.Riesel, see Ref.76, p.120.
79. R.K.Chaturvedi, T.C.Pletcher, C.Zioudrou, and G.L.Schmir, Tetrahedron Letters, 4339 (1970).
80. T.I.Cherepenko, G.A.Golik, V.A.Shokol, V.M.Lopatin, and L.P.Rudenko, Symposium, "Fiziologicheski Aktivnye Veshestva" (Physio-logically Active Substances), Izd.Naukova Dumka, Kiev, 1973, p.6.
81. Yu.V.Shcheglov, V.A.Gilyarov, M.I.Kabachnik, L.S.Kozina, Yu.N.Fadeev, Yu.S.Kagan, and T.A.Raevskaya, USSR P.306 659 (1968); Byul. Izobret., No.15, 238 (1972).
82. L.S.Kozina, Yu.V.Shcheglov, V.A.Gilyarov, and M.I.Kabachnik, "Tezisy Dokladov i Soobshchenii Vsesoyuznoi Konferentsii 'Rezul'taty Nauchno-Issledovatel'skikh Rabot po Sozdaniyu Novykh Pestitsidov, Vendreniyu Ikh v Proizvodstvo i Primeneniyu v Sel'skom Khozyaistve', Sektsiya I" (Abstracts of Reports and Communications at the All-Union Conference on 'The Results of Research on the Synthesis of New Pesticides, Their Industrial Manufacture, and Applications in Agriculture', Section I), Moscow, 1972, p.8.
83. Yu.V.Shcheglov, V.A.Gilyarov, M.I.Kabachnik, L.S.Kozina, Yu.N.Fadeev, D.A.Musikaev, R.S.Mikhailyants, I.G.Vasilevskii, and L.V.Kuz'mina, USSR P.298 317 (1969); Byul. Izobret., No.11, 19 (1971).

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